Synthetic Organic Chemicals

PUBLISHED BY THE

EASTMAN KODAK COMPANY, ROCHESTER, NEW YORK

VOL. IV PUBLISHED MAY, 1931 NO. 4

Cellulose Acetate Plasticizers

BEFORE discussing at any length plasticizers, either general or specific, which may be incorporated in cellulose acetate with beneficial effect, it might be well to review briefly cellulose acetate itself and the advantages of plasticizers.

Cellulose acetate, when completely acetylated, contains theoretically 44.8% acetyl (CH_3CO) or 62.5% combined acetic acid. This material, cellulose triacetate, is often called "chloroform-soluble cellulose acetate" due to its ability to be dispersed by this solvent. Very little technical application of this type has been made to date.

The cellulose acetate which has found the widest use in the technological field is the partially hydrolyzed form in which a portion of the combined acetic acid has been removed. When the acetyl content is reduced thus to between 42.0% and 36.5%, the material becomes soluble in acetone and many other solvents. This is the "cellulose acetate" of the technologist, but it is not a single product with only one set of properties. As the acetyl content is varied from 42.0% to 36.5%, the characteristics change so that a type may be chosen to meet the demands of almost any problem. Viscosity, another very important factor, is also variable and is obtainable in any range from three seconds (approximately equal to quarter-second nitrate) to above 400 seconds, with any desired acetyl content.

The theoretical aspects of the effect of plasticizers in increasing flexibility have not as yet been worked out completely. A short description of one conception of the structure of cellulose acetate in sheet form might be helpful toward a better understanding of their need. Suppose it is considered that the structure of cellulose acetate is like an extremely fine lattice with the particles intertwined. If these particles or micelles are allowed to move against each other as in bending, they are likely to bind and break. An action similar to that of a lubricant in some respects would decrease this tendency and result in a material which would allow much more bending without breakage. This is not, however, the only use of plasticizers. Cellulose acetate may be rendered more resistant to the absorption or transmission of water vapor and, when in sheet form, to changes in dimension due to differences in humidity, by the use of specific materials generally included under the name of plasticizers. In general, plasticizers increase the elongation, increase the flexibility, and decrease the tensile strength. Similarly, transmission of ultra-violet light may be controlled.

It should not be expected that one compound will produce all these desirable characteristics. It is often necessary to change the plasticizer with each problem or to use combinations of plasticizers to obtain the desired result. Al-

though the physical and chemical properties are of great assistance in one's choice, they can by no means be relied upon as determinative.

There are a few definite physical and chemical properties which all compounds to be used as plasticizers should have. The most important property is low vapor pressure. Without this, the softener would soon volatilize and lose its effectiveness. This does not necessarily mean high boiling point, although that also is an advantage. Chemical stability under the conditions employed is essential, as is solubility in the cellulose acetate solvents or compatibility with the solvent-cellulose acetate mixture.

There are generally considered to be three types of plasticizers for cellulose acetate: those which are themselves solvents for cellulose acetate, those which are not, and those which are non-solvents under ordinary conditions, but exhibit solvent action when subjected to high temperatures and pressures. Division may also be made into those which are solids at ordinary temperatures and those which are liquids. In such a general discussion as this, it is only possible to mention certain typical groups.

Chemical structure cannot be relied upon as a basis of the value of a compound as a plasticizer. Attempts have been made in this direction but with the result that the exceptions practically equal those which follow the rule. A great number of esters both of the aliphatic and aromatic series have proved to be satisfactory. Among the solids of this group, triphenyl phosphate is an example of the aromatic series and tributyl phosphate of the aliphatic series. Each has a desirable plasticizing effect, and high stability to heat. Penta erythrytol tetra acetate, although not available for commercial use, is a solid plasticizer which permits of high ultra-violet light transmission. Phenyl carbonate, methyl mandelate, iso-amyl carbamate, and o-cresyl p-toluene sulfonate all produce high stability to heat as well as good flexibility.

Among the liquid plasticizers are tributyrin, which has been found to give a product exceptionally stable to heat, and ethyl phthalate, which in addition is very satisfactory from the standpoint of ultra-violet light transmission. Ethyl malonate and ethyl succinate are especially valuable for inducing flexibility. Benzyl benzoate, ethoxy ethyl phthalate, methyl hydrogen adipate, and ethyl adipate have also been successfully used.

As examples of ketones may be mentioned the aromatic ketone benzophenone, which is a solid, and the cyclic ketone cyclohexanone, a liquid.

Very few of the alcohols have proved successful. Chloretone, or trichlorotertiary butyl alcohol, is one which has, however. Among the ethers it might be well to mention the two related liquids, benzyl ether and diphenyl ether, both of which are in the aromatic series.

Still another type of compound is that in which the amino group is present; ethyl acetanilide and m-toluene sulfonethyl amide are examples.

Paraldehyde, a polymer of acetaldehyde, is of value for special purposes. Mono-chloronaphthalene and n-butyl sulfone are both considered to possess distinct advantages.

Only a relatively small number of the many compounds known to produce beneficial effects when added to cellulose acetate have been included here. Examples of various types have been chosen in an attempt to give an idea of the extremely wide latitude that is possible in the selection of a plasticizer. Continual research is increasing this list.

EDITOR'S NOTE—The foregoing information is given merely as an aid to experimental work and not as a recommendation to employ such compounds commercially in violation of any patents or patent rights which may now or hereafter exist thereon.

Laboratory Stirrers

THE importance of stirring in analytical procedures as well as in other inorganic operations has recently been emphasized. An efficient stirrer is also very useful in the organic laboratory. The centrifugal model shown in Figure 2 has been found very satisfactory for general use. It can be easily and quickly made by anyone familiar with blowing glass.

The stirrer is supported or guided by a piece of glass tubing which is slipped over the shaft and attached by a clamp to some rigid support. The glass tube can be lengthened so as to project below the surface of the solution, thus forming a liquid seal. As the stirrer is rotated, the liquid is drawn through the opening in the bottom and thrown vigorously to the side of the vessel. If, instead of joining the stirring rod directly to the motor, a short glass rod connected by rubber tubing at each end is inserted, much of the vibration is avoided.

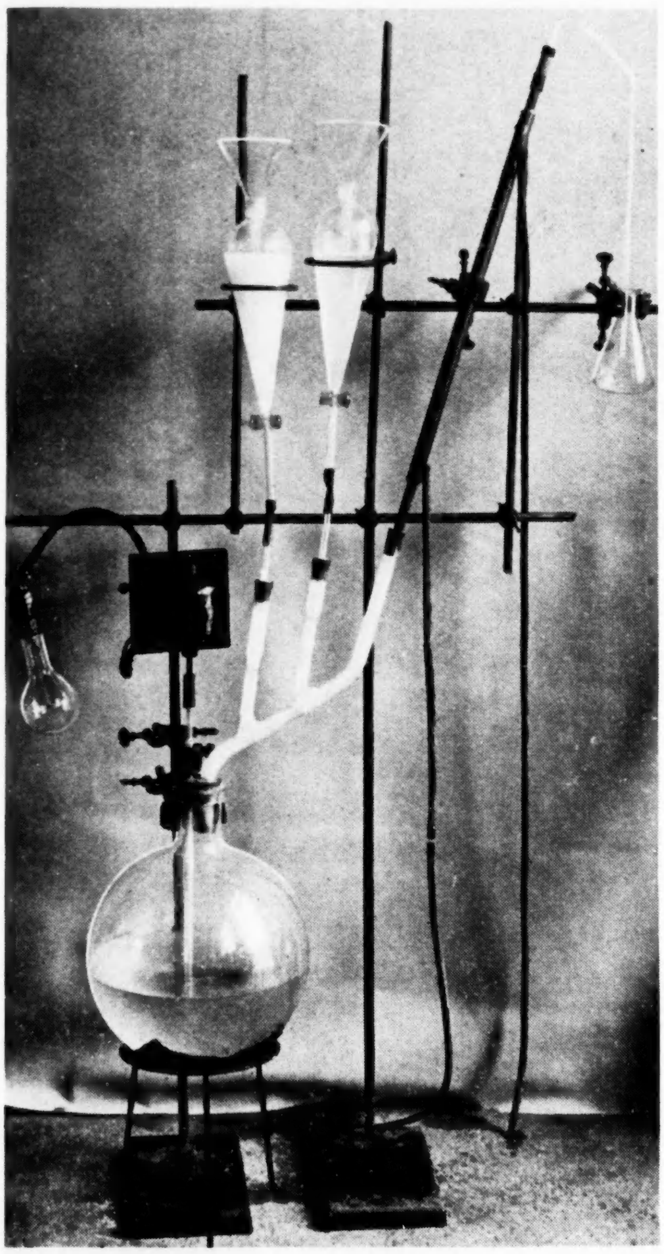

FIGURE 1—*Apparatus for hydrolysis of esters*

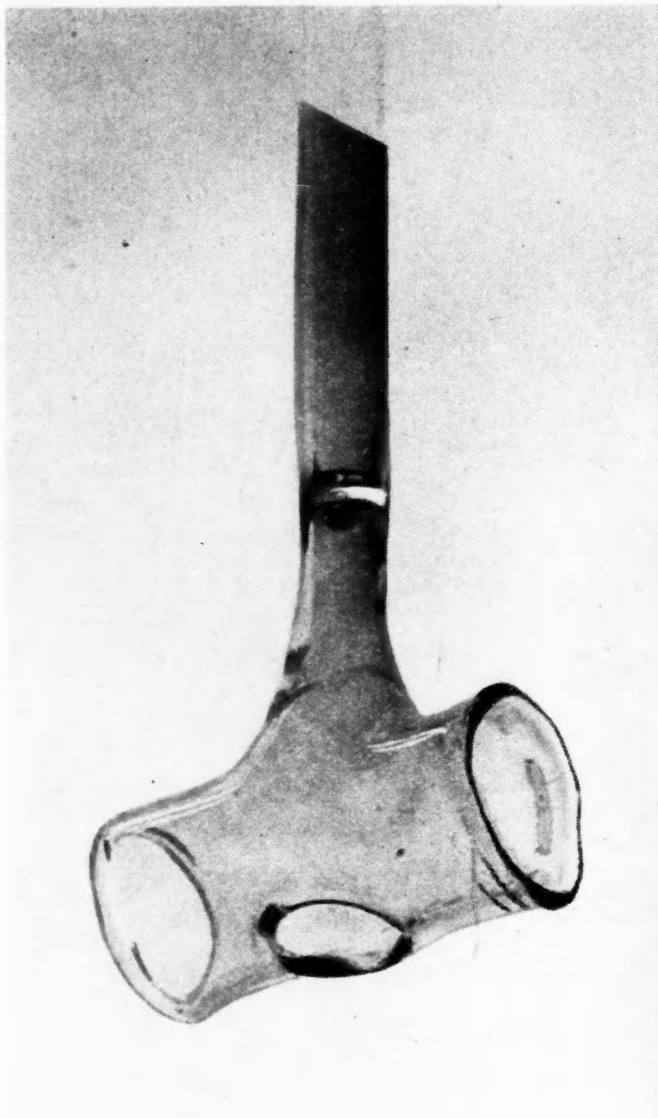

FIGURE 2—*Centrifugal stirrer*

The illustration, Figure 1, shows an assembly for hydrolyzing esters in which stirring plays an important part. One of the best ways of preparing pure aliphatic acids is to fractionate the methyl esters since their boiling points are more widely separated than those of the acids themselves. The methyl ester is then hydrolyzed and the pure acid separated by acidifying and washing. In attempting to carry out these hydro-

lyses without vigorous and continued stirring, local heating can very easily get out of control, causing danger from fire. Through the use of a stirrer, such as the one described, the ester and alkali can be added to the reaction mixture at such a rate that the operation will proceed smoothly, carried on by its own heat of reaction.

Eastman Organic Chemicals as Analytical Reagents

XIX Reagents for Cadmium.

HEXAMETHYLENETETRAMINE ALLIODIDE

Everard: Chem. Abs. *24*, 311 (1930)

Cadmium can be detected microchemically by the formation of a characteristic precipitate when a drop of the dilute metal solution is placed in contact with a drop of a 10% aqueous solution of the above reagent. The complex precipitate contains 11.44% cadmium after drying at 105°. It can be used as the basis for a gravimetric method.

ETHYLENEDIAMINE

Spacu and Suciu: Z. Anal. Chem. *77*, 340 (1929)

The reagent used is a copper salt formed by heating on the water bath copper nitrate and ethylenediamine in the molecular ratio of 1:2. As soon as crystallization begins the solution is cooled, filtered, and the crystals washed with alcohol and ether.

The dilute neutral cadmium solution is treated with an excess of potassium iodide, heated to boiling, then mixed with a hot concentrated solution of the reagent described. A crystalline blue-violet precipitate containing 13.99% cadmium is obtained.

ALLYLTHIOUREA

Gutzeit: Helv. Chim. Acta, *12*, 718 (1929)

This reagent consists of a 5% solution of allylthiourea to which is added, just before use, 5% of a caustic soda solution (30%). When heated with a cadmium solution, a yellow precipitate is obtained.

PYRIDINE

Spacu and Dick: Z. Anal. Chem. *73*, 279 (1928)

About 100 cc. of the neutral cadmium solution is heated to boiling and treated with 1 gm. of ammonium thiocyanate and 1 cc. of pyridine. The precipitate formed on cooling is filtered and washed with cold water, alcohol, and ether, each containing diminishing amounts of the precipitants. The compound contains 29.07% cadmium.

New Eastman Organic Chemicals

The following chemicals have been added to our list since the last issue of this bulletin. Over 2,800 items are now in stock.

*β'–Butoxy–β–ethoxyethyl Acetate
*n–Butyl α.α'–Dibromosuccinate
*n–Butyl Maleate
*β–Di–n–butylaminoethyl Alcohol
*β–Di–n–butylaminopropyl Alcohol
*γ–Di–n–butylaminopropyl Alcohol
*Diethylene Diacetate
*Dipropanolamine
*β'–Ethoxy–β–ethoxyethyl Acetate
*β–Ethoxyethyl Glycollate
*Ethyl N–n–butylcarbamate
Ethyl n–Butylethylmalonate
*Ethyl α.α'–Dibromosuccinate
*Ethyl N.N–Di–n–butylcarbamate
Ethyl *l*–Methyl–n–butylmalonate
Ethyl Phenylethylmalonate
Ethyl iso–Propylethylmalonate
o–Hydroxydiphenyl Sodium Salt
*Propanolamine
*n–Propyl Carbamate
*n–Propyl α.α'–Dibromosuccinate
*n–Propyl Maleate
*Triethylene Diacetate
*Tripropanolamine

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